

**Measurements of H₂¹⁶O line frequencies and strengths: 11610 to
12861 cm⁻¹**

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Tables 3

Abstract

High resolution spectra of H₂¹⁶O vapor covering the region from 11610 to 12861 cm⁻¹ were used to determine experimental values of line positions and strengths of 933 lines which include vibration-rotation transitions in the (211)-(000), (131)-(000), (310)-(000), (112)-(000), and (031)-(000) bands from which rotational energy levels in the (211), (131), (310), (112), and (031) vibrational states were obtained. The line strengths and frequencies reported here are considered to be a marked improvement over the values listed on the 1986 edition of the HITRAN database and a preliminary listing from this work has been included in the 1993 HITRAN edition.

I. INTRODUCTION

In two recent papers(1,2) by this author, high resolution measurements of line positions and strengths of $H_2^{16}O$ observed in the 5750 to 7965 cm⁻¹ region(1) and comparable measurements of $H_2^{17}O$ and $H_2^{18}O$ in the 6600 to 7640 cm⁻¹(2) were reported. The present study is an extension of the previous two investigations in which experimental line positions and strengths of $H_2^{16}O$ in the 11610 to 12862 cm⁻¹ were derived covering vibration-rotation transitions of the (131)-(000), (310)-(000), (211)-(000), (112)-(000), and (013)-(000) bands.

Only one study has reported water vapor measurements in this spectral region. Adler-Golden et al.. (3) measured the line widths of 10 lines in the 12141 to 12238 cm⁻¹ region and determined the line strengths of two of these lines located at 12195.19 and 12212.07 cm⁻¹. The 1986 edition of the HITRAN database(4) contained line frequencies and strengths in this spectral region which were based upon unpublished results; the latest HITRAN listing(5) includes preliminary results from this study.

II. EXPERIMENTAL DETAILS

The spectra were recorded at the Kitt Peak National Observatory using the Fourier transform spectrometer (FTS) located at the McMath solar telescope facility. The experimental conditions and extent of the measurements are given in Table 1. The table lists the unapodized spectral resolution, sample pressures, temperatures and path lengths used for each of the four

runs as well as the relative isotopic abundances of $H_2^{16}O$, $H_2^{17}O$, and $H_2^{18}O$. The bottom portion of the table lists the frequency extent of the measurements observed in the five bands.

It was noted in the two other H_2O studies(1,2) that absorption due to the $H_2^{16}O$ content in the open spaces between the IR source and vacuum tank, which enclosed the FTS, the small amount of water vapor (50 to 200 μ in total pressure) in the vacuum tank were observed as added contributions to the stronger $H_2^{16}O$ absorption, in the spectra. However, for the present study, the stronger lines were observed without those added contributions due to the relative weakness of all of the lines in this spectral region. Further calculations also confirmed this finding.

All data were obtained with the sample temperatures near or at room temperature (296K) as shown in Tab. 1. Sample temperatures were inferred from readings of one or more thermistor probes in thermal contact with the absorption cell walls while the total sample pressures were measured with a Baratron gauge. The measured pressures and temperatures were monitored continuously during the spectral runs with estimated uncertainties in the readings of 0.5% and 1.0K, respectively. Each FTS run consisted of at least eight co-added interferograms collected over a period of approximately 50 min. The composite interferograms were transformed into spectral data at the Kitt Peak facility.

The line centers were measured using two computer programs. One, labeled linefinder, determines line-center positions and relative absorption peaks by a method that uses first and second

derivatives of the spectrum. The second uses the technique of non-linear least-squares (NLLS), in which absorption line positions, strengths, linewidths and continuum parameters are fitted simultaneously in an interactive mode. The latter technique was used to determine experimental values of line strengths.

The Measured line positions obtained by both techniques were calibrated and corrected by reference to available $H_2^{16}O$ calibration frequencies. The spectral runs extended up to 16,000 cm^{-1} and $H_2^{16}O$ frequencies measured (but not reported here) from 13,200 to 16,000 cm^{-1} were normalized to reported frequencies given by Mandin et al. (6) and this method of calibration was applied to the lower spectral region (11610 to 12862 cm^{-1}) . They(6) estimated the absolute uncertainty in their line positions to be $\pm 0.002 \text{ cm}^{-1}$ for the strong and well-isolated lines which were the ones used in the present study for calibration purposes. Therefore the estimated absolute uncertainty in the line positions measured in this study is, at best, $\pm 0.002 \text{ cm}^{-1}$. However, the precision of the frequency values vary from $\pm 10^{-4} \text{ cm}^{-1}$ for the strongest and well-isolated lines to $\pm 0.005 \text{ cm}^{-1}$ for the weakest and/or most blended measurements.

III. ENERGY LEVELS

In an earlier report(7), the ground state and (010) state $H_2^{16}O$ rotational energy levels and associated, estimated uncertainties were determined from microwave, far infrared and combination difference frequencies. The combination difference frequencies were derived from experimental transition frequencies observed in

the region from 1000 to 4500 cm⁻¹. The measured line positions obtained in the present study of the five ground state bands were used along with the ground state term values to derive values of rotational energy levels and associated, estimated uncertainties in the upper vibrational states by adding to each measured transition frequency of a band, the appropriate ground state level. These results were weighted and then averaged for each level. Table 2 lists values of the rotational energy levels obtained in this work for the (211), (131), (310), (112), and (013) vibrational states along with the associated uncertainties.

IV. RESULTS

Table 3 is a listing of the lines used in the analysis. Entries for the table include the observed line position, observed minus computed, o-c, line position, rotational quantum assignments, observed strength, estimated uncertainty in the measured strength, %S, the ratio, R, of the observed line strength value to that given in the 1986 version of the HITRAN database (4), and the upper vibrational state of the band. In order to compute values of R, the strength values given in ref. (4) were converted from cm⁻¹/mol·cm⁻² to cm⁻²/atm. by applying a factor of 2.48 × 10¹⁹.

The observed line positions are given to 3, 4, or 5 places past the decimal which is an indication of the accuracy of the measurements. Obviously, the most accurate measurements are those with the values given to 5 places past the decimal. An asterisk next to the line position value denotes a doubled absorption for

which the two transitions were not adequately resolved in the spectra to determine their respective parameters using the NLLS program. The quantum assignment given represents the stronger transition and the value of the observed strength is the sum of the strengths of the two comparable transitions. Values of o-c were derived from the term values given in Table 2 and the ground state values given in ref. (7) and the observed positions. Entries with %S = 15% represent line strength uncertainties of as much as 60% to possibly less than 10%. This range of uncertainty arises from one or more of the following reasons: (a) blending, (b) weakness of the transition intensity, and (c) poor agreement between the values derived from the various spectra.

Several of the measured lines in Table 3 were not assigned as noted by the absence of quantum and band assignments in the entries for these features. These lines could be weaker transitions of the bands included in this analysis or transitions of additional bands that were not considered in this study such as the (051)-(000), (230)-(000) , (150)-(000) and (032)-(000) bands.

As noted in the introduction, Adler-Golden (3) measured the line strengths of two lines located at 12195.19 and 12212.07 cm⁻¹ which are the 2 0 2 - 1 0 1 and 3 0 3 - 2 0 2 rotational transitions, respectively, of the (211)-(000) band. Their line strength values were normalized to a temperature of 296 K with values of 9.87×10^{-4} cm⁻²/atm. and 4.24×10^{-4} cm⁻²/atm. for the two lines (converted from cm⁻²/mol-cm) which are 13% and 11% , respectively, higher than the values obtained in this study.

Their(3) measurements were obtained using an 817-824 GaAlAs diode laser with the heated (330-540 K) water vapor contained in a 40.3 cm long cell with sample pressures up to 0.13 atm.

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Table 1. Experimental conditions

run no.	res. ^a	sample	sample	path (m)	per cent abundance		
		press. Torr	temp. (K)		H ₂ ¹⁶ O	H ₂ ¹⁷ O	H ₂ ¹⁸ O
1	0.011	1.15	297	98	99*9	0.036	0.203
2	0.011	2.12	297	196	99.9	0.036	0.203
3	0.011	10.1	297	433	99.9	0.036	0.203
4	0.011	16.1	297	433	99.9	0.036	0.203

a. Unanodized spectral resolution in cm-1

Extent of measurements in cm-1

band	measurements
(211)-(000)	11844 - 12540
(310)-(000)	11830 - 12414
(131)-(000)	11610 - 12245
(112)-(000)	12102 - 12670
(013)-(000)	12321 - 12752

Table 2. Rotational energy levels of the (211), (131), (310), (112), and (013) vibrational states of $H_2^{16}O$ in cm^{-1} . Estimated uncertainties (precision) in $\text{cm}^{-1} \times 10^5$

J K _a K _c	(211)	(131)	(310)	(112)	(013)	J K _a K _c
0 0 0	12151.25485 40	11813.20720 10	12138.86792 60	12407.65212 40	12565.00712 10	0 0 0
' 1 0 1	12173.76445 10	11836.45590 20	12162.10704 40	12430.52310 30	12588.15600 30	1 0 1
' 1 1 1	12187.81588 20	11859.11855 50	12176.43940 30	12444.09440 40	12600.57510 30	1 1 1
' 1 1 0	12193.34567 30	11865.28735 10	12181.59822 40	12449.64629 30	12606.26272 40	1 1 0
2 0 2	12218.98695 15	11881.79890 40	12206.34800 300	12474.85040 40	12632.86725 20	2 0 2
2 1 2	12227.88065 40	11899.40795 50	12215.57845 30	12484.26280 30	12641.20504 40	2 1 2
2 1 1	12244.39995 15	11917.84850 40	12232.49944 50	12500.88940 50	12658.23720 40	2 1 1
2 2 1	12285.36300 40	11983.97050 50	12274.40555 20	12541.68487 10	12695.10100 80	2 2 1
2 2 0	12286.72'516 15	11985.06538 30	12275.26412 40	12543.05141 30	12696.65110 40	2 2 0
3 0 3	12282.16060 15	11947.21500 50	12269.78937 30	12538.38968 35	12696.73710 20	3 0 3
3 1 3	12287.24/909 10	11959.19600 15	12275.19360 30	12543.70755 30	12701.23420 20	3 1 3
3 1 2	12319.85755 10	11995.73160 60	12308.11735 100	12576.65199 20	12734.91950 15	3 1 2
3 2 2	12353.73126 25	12053.75170 40	12342.95773 40	12610.27800 30	12764.66130 10	3 2 2
3 2 1	12360.00400 40	12058.95690 25	12348.85785 50	12616.58930 50	12771.71020 20	3 2 1
3 3 1	12435.33510 30	12174.51548 15	12425.46490 300	12691.42900 80	12839.84825 20	3 3 1
3 3 0	12435.55395 15	12174.63789 50	12425.66312 40	12691.71425 40	12840.12805 10	3 3 0
4 0 4	12362.86290 30	12030.62014 20	12348.80651 300	12619.75381 50	12777.50162 30	4 0 4
4 1 4	12365.28305 25	12037.87110 40	12353.22024 50	12621.74160 30	12779.93383 20	4 1 4
4 1 3	12418.08440 50	12097.32940 40	12408.65657300	12675.36700 40	12834.47578 30	4 1 3
4 2 3	12443.76750 40	12145.81874 30	12433.31610 50	12700.53032 40	12856.00500 50	4 2 3
4 2 2	12460.17570 40	12160.07010 40	12446.63048 500	12717.05906 80	12874.10585 40	4 2 2
4 3 2	12528.75'720 60	12269.60200 50	12519.01710 40	12785.45753 20	12935.37402 20	4 3 2
4 3 1	12530.20600 40	12270.43850 40	12520.32724 50	12786.60320 30	12937.18870 30	4 3 1
4 4 1	12637.86555 20	12426.91158 60	12629.99009 50	12893.32010 50	13034.63658 80	4 4 1
4 4 0	12637.89850 80	12426.95140 60	12630.02239300	12893.32080 50	13034.67961 40	4 4 0
5 0 5	12460.36526 6 0	12130.78700 100	12447.02339300	12716.31380 50	12875.52776 50	5 0 5
5 1 5	12461.39/359 40	12134.82420 20	12447.50109 100	12717.80770 60	12876.76909 80	5 1 5
5 1 4	12536.49205 15	12218.716432300	12528.30140 50	12794.76100 50	12954.30690 40	5 1 4
5 2 4	12554.87985 25	12259.46840 50	12544.98086 30	12811.53256 60	12968.11470 30	5 2 4
5 2 3	12586.59530 25	12288.57657300	12575.02800 60	12843.76960 40	13002.84600 50	5 2 3
5 3 3	12645.32987 40	12388.32420 40	12637.14757300	12902.44767 30	13054.37910 30	5 3 3
5 3 2	12650.59082 10	12391.50775 50	12640.54942 60	12907.32600 80	13060.74280 60	5 3 2
5 4 2	12755.13590 6 0	12545.69620 80	12747.81055 20	13010.77974 80	13157.07011 50	5 4 2
5 4 1	12755.39J10 20	12545.87028400	12748.04070 60	13010.83753 80	13157.34128 300	5 4 1
5 5 1	12892.32686300	12737.20220 80	12883.59728300	13143.64851 300	13277.82600 80	5 5 1
5 5 0	12892.32679 300	12737.20400200	12883.63610 30	13143.56551 70	13277.82800 300	5 5 0
6 0 6	12574.737613 60	12247.43040 30	12562.36721 300	12830.84930 20	12W0 .50775 30	6 0 6
6 1 6	12575.20462 25	12249.62061 20	12562.84064 40	12831.52200 50	12989.63050 50	6 1 6
6 1 5	12678.17772 1 5	12368.20474 30	12666.54176300	12934.27370 40	13091.86720 60	6 1 5
6 2 5	12683.24797 40	12394.09750 40	12671.73350 25	12942.33927 50	13099.99474 100	6 2 5
6 2 4	12737.55660 50	12441.60390 100	12726.72920300	12996.75251 300	13155.86401 10	6 2 4
6 3 4	12784.40645 20	12527.88420300	12775.07200500	13042.34860 40	13196.15570 60	6 3 4
6 3 3	12797.94395 40	12538.92150 130	12788.56876300	13054.54200 60	13211.91244 50	6 3 3
6 4 3	12896.05670 60	12689.06029300	12889.69620 100	13152.05600 300	13302.32551 300	6 4 3
6 4 2	12897.23440 40	12689.44796 100	12890.63010 50	13152.61609700	13303.47661 40	6 4 2
6 5 2	13033.43280 40	12881.16900 500	13024.31331 300			6 5 2
6 5 1	13033.46086 50	12881.17096 50	13024.31721 50			6 5 1
6 6 1	13200.58409 300	13092.76409 80			13567.22160 200	6 6 1
6 6 0	13200.58409 300	13092.76409 8 0			13567.22160 200	6 6 0
7 0 7	12706.17340 30	12381.43207400	12692.21186 50	12%2.37960 50	13122.64109 40	7 0 7
7 1 7	12706.85481 25	12381.98750 80	12692.47674 300	12962.98329 80	13122.68427 20	7 1 7
7 1 6	12831.97315 35	12545.47182 300	12819.59433300	13088.93993 300	13245.86182 50	7 1 6
7 2 6	12833.57480 40	12548.82206 80	12822.95438300	13099.77482300	13251.40306 40	7 2 6
7 2 5	12910.76255 20	12610.39650300			13330.48340 60	7 2 5
7 3 5	12945.03730 60	12692.97315 30			13362. W727 60	7 3 5
? 3 4	12972.43710 40	12724.57997300			13390.42127 60	7 3 4
7 4 4	13060.37710 3 0					7 4 4
7 4 3	13064.23220 80					7 4 3
7 5 3	13198.19280 30					7 5 3
7 5 2	13198.34550 60					7 5 2
7 6 2	13365.03510 60					7 6 2
7 6 1	13365.03510 60					7 6 1
7 7 1	13566.16938 300					7 7 1
7 7 0	13566.16938300					7 7 0

Table 2 continued

J	K _a	K _c	(211)	(131)	(310)	(112)	(013)	J	'a	'c	
8	0	8	12855.24095 15	12530.76964 80	12841.74617 300	13112.16421 300	13272.01264 50	8	0	8	
8	1	8	12854.16035 15		12842.03321 60	13111.62524 80	13272.01921 300	8	1	8	
8	1	7	12999 .12110 10				13416.22600 200	8	1	7	
8	2	7	13001.51625 25				13419.55685 20	8	2	7	
8	2	6	13103.48730 30				13523.79642 50	8	2	6	
8	3	6	13126.70450 25		13121.94053 60		13559.71238 300	8	3	6	
8	3	5	13172.714.58 15				13594.51871 300	8	3	5	
8	4	5	13247 .31270 30					8	4	5	
8	4	4	13257.44665 40					8	4	4	
8	5	4	13386.56160 40					8	5	4	
8	5	3	13387.17955 15					8	5	3	
8	6	3	13553.675117 40					8	6	3	
8	6	2	13553.675117 40					8	6	2	
8	7	2	13756 .23233 40					8	7	2	
8	7	1	13756.23233 40					8	7	1	
8	8	1	13965 .53235 300					8	8	1	
8	8	0	13965 .53235 300					8	8	0	
9	0	9	13019 .39410 50				13438.56004 60	9	0	9	
9	1	9	13020.09800 10				13438.57176 60	9	1	9	
9	1	8	13187.085107 50				13603.68577 60	9	1	8	
9	2	8	13187.122197 15				13603.55403 60	9	2	8	
9	2	7	13311.47627 40					9	2	7	
9	3	7	13327.67240 40				13747.12706 300	9	3	7	
9	3	6	13396 .08977 80					9	3	6	
9	4	6	13457.83952 25					9	4	6	
9	4	5	13477.94785 40					9	4	5	
9	5	5	13598.33120 50					9	5	5	
9	5	4	13599.91870 300					9	5	4	
9	6	1 i	13763.70521 300					9	6	4	
10	0	10	13202.27333 10				13622.36521 100	10	0	10	
10	1	10	13202.21503 20				13622.36457 100	10	1	10	
1	0	1	9	13386.68585 30			13808.70149 60	1	0	1	9
1	0	2	9	13386.91451 60			13808.29711 60	1	0	2	9
1	0	2	8	13545.80165 40				1	0	2	8
1	0	3	8	13555.03194 50				1	0	3	8
1	0	3	7	13639.75987 300				1	0	3	7
10	4	6	13726.040154 200					1	0	4	6
11	0	11	13401.92500 500				13822.89600 200	11	0	11	
11	1	11	13401.92689300				13822.89560 100	11	1	11	
11	1	10	13609.00610 60					11	1	10	
11	2	10	13607.89720 40				14028.06360 80	11	2	10	
12	0	12	13618.49016300				14038.99916 300	12	0	12	
12	1	12	13618.49016 300				14038.99916 300	12	1	12	
13	0	13	13852.01490300					13	0	13	
13	1	13	13852.01539300					13	1	13	
14	0	14	14102.35655 60					14	0	14	
14	1	14	14102.35655 60					14	1	14	
15	0	15	14369.86485 100					15	0	15	
15	1	15	1514369.86485 100					15	1	15	

